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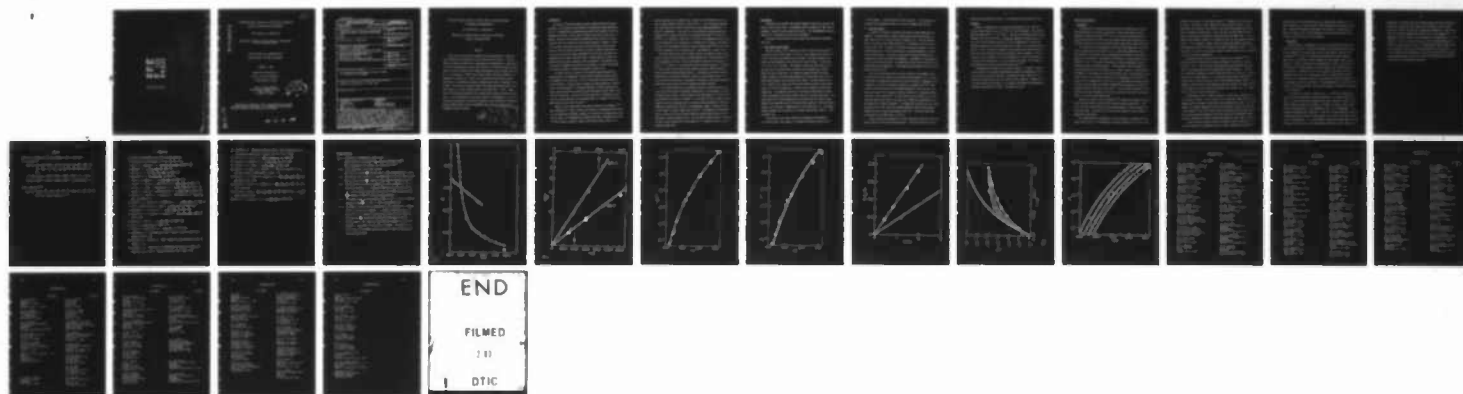
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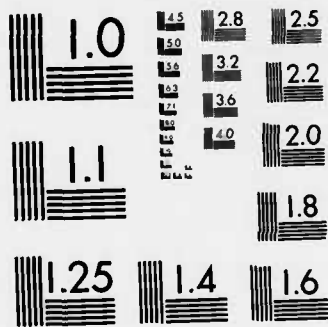
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Vibrational Energy Transfer at a Gold Surface in Reacting
Systems. Cyclobutene and Nitromethane

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Vibrational Energy Transfer at a Gold Surface in Reacting Systems.

Cyclobutene and Nitromethane[†]

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Abstract

Single collision excitation probabilities were measured for cyclobutene and nitromethane on polycrystalline gold plane and wire surfaces. Transport above the reaction thresholds for isomerization and decomposition, respectively, for the two substrates was used as the criterion of vibrational energy transfer. Several different seasoning and processing procedures of the surfaces were tested. For cyclobutene, a defect from strong collider transition probabilities appeared only above 550 K - 600 K, which signifies that the energy transfer efficiency at a treated gold surface is greater than that at a seasoned silica surface. The vibrational energy transfer efficiency declined above 600 K and fell abruptly to a quasi-constant value in the range 900 K - 1100 K. Above 1100 K the differences between various conditioned surfaces diminished progressively. Unlike cyclobutene, and earlier studies of nitromethane on silica surfaces where reproducible non-catalytic behavior could be attained, nitromethane on gold showed apparent catalytic phenomena which the various conditioning treatments failed to repress.



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Introduction

The study of vibrational energy transfer between molecules and metal surfaces is of continuing interest both for theoreticians and experimentalists.¹⁻³ Rosenblatt⁴ has studied energy transfer efficiencies at room temperature on different "dirty" metal surfaces, particularly iron, by an ingenious vibrating surface method and obtained relative values for energy transfer involving internal and translational degrees of freedom. He and his co-workers found that hydrocarbons exhibited larger energy transfer facility than did diatomic molecules; for heavier paraffin hydrocarbons (C_4-C_8) the vibrational energy accommodation coefficients approached 0.9, presumably due to longer residence times. Related results at higher temperature have also been reported by Foner and Hudson.⁵ They measured the vibrational accommodation coefficient of *n*-butane on a "dirty" polycrystalline platinum ribbon at 1000°C and reported a value of 0.05.

Our recent series of studies by the Variable Encounter Method⁶ has been devoted to the phenomenon of gas-surface vibrational energy transfer on seasoned silica surfaces at a level of vibrational excitation above reaction threshold. Single collision systems have been examined as a special case of the VEM method.^{7,8} The energy transport of reactant molecules to levels above the reaction threshold can be observed most simply under single collision conditions. For multi-collision conditions, the energetic distribution of excited molecules is an average effect of a sequence of collisions. Both conditions have their own uses.⁸

Several of our studies dealt with energy relaxation by cyclobutene⁷⁻¹⁰ and nitromethane.¹¹ Energy transfer efficiencies at seasoned pyrex and fused silica surfaces were examined. Because of its polarity, a larger energy transfer efficiency for nitromethane was expected and found. Amorebleta and Colussi¹² have recently reported a study of vibrational energy transfer in an

n-octane-seasoned silica system using a variant of the VEM method and a diagnostic energy technique similar to that of ref. 5. Their evaluated accommodation coefficient had a value of 0.66 at 350 K and decreased approximately linearly with temperature. Their result is quite different from the approximate strong collider character obtained for cyclobutene below 450 K⁷ by Arakawa et al.^{8,10} It is of interest to note that if one plots the accommodation coefficients against temperature for cyclobutene on a seasoned silica surface, calculated on the basis of the Boltzmann-Exponential energy transfer model,^{8,9} then the result of Foner and Hudson fits on the same curve. The comparison is shown in Fig. 1.

One might expect that a metal surface would be a stronger collider because of the variety of possible energy relaxation mechanisms, including phonon, hole pair and plasmon excitation, that are postulated to function for molecules on metals.¹³⁻¹⁵ However, it is possible that the relaxation process on a seasoned or "dirty" metal surface might simply resemble the better known¹⁶ gas phase, molecule-molecule energy exchange behavior. One molecule of the pair would be represented by the graphitic/polymeric covering on the seasoned surface. Of course, gas/solid interaction is presumably not subject to the angular momentum conservation restrictions found for two-body gas phase transfers.

In the present paper we have extended the study of surface variation to a single collision study of cyclobutene isomerization to 1,3-butadiene on a polycrystalline gold surface. We have chosen to use gold because it is one of the most amenable of the metallic elements. In the form of finely divided particles supported on oxide substrate, gold can catalyze some hydrogenation, isotope exchange and isomerization reactions of hydrocarbons; however, the massive form of the element is usually catalytically inert.¹⁷ The behavior of nitromethane, which in the earlier work was found to exhibit greater sensitivity to surface conditions, has been studied as well. We find that the gold surface is relatively inert in the isomerization of cyclobutene to 1,3-butadiene but not in nitromethane decomposition.

Experimental

Cyclobutene was obtained from Columbia Chemicals (99.9% pure) and was used without further purification. Nitromethane (Aldrich Chemical Co. 99%, spectrophotometric grade) was used without purification. Gas chromatographic analysis showed that it contained less than 0.5% nitroethane.

Two types of polycrystalline gold surfaces and experimental arrangements were used.

A. Gold plated finger reactor

The basic design of this reactor was similar to that of previous work.⁷ A stainless steel, hollow finger, 3.8 cm o.d., was located at the center of a 5-liter flask which was immersed in an ice bath. The outer surface of the finger was electroplated (over nickel) with a layer of gold ($> 99.8\%$ pure), $\approx 2.5 \times 10^{-3}$ cm in thickness. The length of the active section was 5.9 cm, and the area of the gold surface including the flat bottom was $\approx 80 \text{ cm}^2$. Above the active region was a 1 cm length of plated thin-wall (to reduce thermal conduction from the bottom heated part) section which led to a 3 cm water-cooled length of the stainless steel finger. The inner region of the 5.9 cm length of the finger was filled with a Pb-Sn-Bi eutectic alloy and was used as an internal heating bath. A blade stirrer produced a uniform bath temperature. The temperature profile of the bath was measured by a chromel-alumel thermocouple which moved inside a thin wall stainless steel tube. This design gave fairly uniform temperature distribution over the finger surface. Except for the uppermost part of the gold surface adjacent to the thin-walled section, the variation of temperature over the surface was $\pm 4^\circ$. The average distance between the hot surface of the finger and the wall of the 5-l flask was about 7 cm.

The surface of the finger reactor was processed by three methods:

- a) oxidation with 1 torr oxygen; b) oxidation followed by reduction with

1 torr hydrogen; c) seasoning with 10^{-2} torr reactant. All the processing procedures were conducted at 600 K to 700 K and repeated anew each day.

B. Gold wire reactor

A length of 26 gauge fine gold wire was drawn by Speyer Metallurgy Co., Seattle. A U-shaped double length of gold wire was hung longitudinally on small glass hooks in a glass cylinder of diameter 9 cm. The wire diameter was 0.1 mm and its total length was 69.5 cm. The geometric surface area of this wire was 2 cm^2 . The ends of the gold wire were spot-welded to a nickel-coated tungsten rod. The wire was heated to a maximum temperature of 1200 K by resistive heating. The electric resistance was found by measuring the voltage and current with Keithley voltammeters. Adjustment of the temperature of the wire was fast and easy. The temperature of the glass cylinder wall was maintained at room temperature. The average distance between the wire and the glass cylinder was 4 cm.

Due to end losses there were two cooler regions on the uppermost parts of the gold wire; the length of each region was approximately 4 cm. In order to estimate the temperature distribution over this length, we resorted to the treatment of a similar circumstance reported for tungsten wire.^{18,19} After correction for the end effect, the average temperature of the wire was calculated from a chart of the specific electric resistance vs. temperature drawn from data in the literature.²⁰ To check the value and uniformity of the temperature along the main part of the gold wire, temperature measurements were also made with an optical pyrometer. The temperature variation over the length of the wire was $\pm 25^\circ$, while the average temperature given by the pyrometer agreed with the resistance measurements within 10° . The latter measurement was adopted for the temperature of the wire.

Similar processing procedures as for the finger were used except that they were carried out at 100-fold lower pressures. It was found that a half-hour

seasoning gave reproducible results. The procedure was carried out at 1100 K.

Procedure

Before a cyclobutene run, the reactor was evacuated to $\approx 3 \times 10^{-6}$ torr for the finger reactor and $1-2 \times 10^{-6}$ torr for the wire reactor. The substrate reaction pressure was $\approx 1-2 \times 10^{-4}$ torr. The reaction fraction was 0.5% to 80% (finger) and 0.5% to 50% (wire). The average temperature change during a run was $\pm 0.5^\circ$ for the shortest run and $\pm 4^\circ$ for the longest one. The reaction temperatures were varied over the range of 425 - 668 K, for the finger reactor, and 525 - 1150 K, for the wire reactor, so that there was an overlap region in which the results obtained from the two reactors could be compared. The reaction mixture was collected in a liquid nitrogen trap. Analysis was made with a squalane SCOT column and FID. No side reaction was found. In all details, the procedure was similar to that described earlier.^{7,10}

Nitromethane was studied only in the wire reactor. As before,¹¹ acetonitrile was used as an internal standard against which the disappearance of substrate could be accurately measured. No attempt was made to monitor all of the product species which, for this system, are very numerous. Separation of the reaction products was made on a 1-m column of 3mm copper tubing packed with Porapak Q and maintained at 150°C. The detector was FID.

Results and Discussion

Cyclobutene

The molecules of cyclobutene energized above the threshold have a greater than 99% probability of reaction during their flight time from the surface, according to RRKM calculations.⁸⁻¹⁰ Collision of the activated molecule with the bath gas during the flight time can be neglected and the unimolecular isomerization reaction is close to the second order region under present conditions.

The isomerization of cyclobutene on the gold finger obeyed the first order rate law; sample curves are shown in Fig. 2. Within the experimental error, no difference in the results was noticed between the different processing procedures for the surface. The apparent rate constant k is plotted against temperature in Fig. 3. Some points, especially at higher temperatures, are the average of three to four measurements. The experimental reaction probability P_c was obtained by use of the equation, $P_c = 4 V k / S \bar{c}$, where V is the volume of the reactor, S is the area of the hot gold surface, and \bar{c} is the average translational velocity of the reactant molecules at the temperature of the cold wall. A plot of P_c vs. temperature is given in Fig. 4; two theoretical strong collider P_c curves are also shown, which were calculated for two values of the reaction threshold energy,²¹ 32.0 and 32.4 kcal mol⁻¹. The two values correspond to two different activated complexes; Elliott and Frey prefer the latter value although there is little to choose between them.

The earlier studies in this laboratory^{7,9,10} showed that seasoned pyrex and silica surfaces exhibit strong collider character near and below 400 K. From Fig. 4, one can conclude that the gold surface behaves as an even stronger collider than those. The defect from strong collider behavior is only evident at temperatures above 600 K.

The isomerization of cyclobutene in the wire reactor also obeyed the first order rate law (Fig. 5). The measured P_c values are shown in Fig. 5 or 6. When

compared with the data for the finger reactor, it is apparent that the two sets of values in the lower, overlap temperature region concord quite well. Some differences arise however in the effect of the processing procedure on the gold wire at intermediate temperatures. As was the case in earlier work with hydrocarbons, the cyclobutene seasoned surface again gave the lowest rate. The oxidized surface seemed to behave as a stronger collider than the seasoned (reduced) surface. It is noteworthy, however, that all seasoning procedures converge on the same energy transfer efficiency at the highest temperatures (1100 K - 1150 K); this leads us to believe that surface catalytic reaction effects are not important in the wire activation experiments.

Some analogy may be drawn with work of Somorjai and co-workers.^{22,23} His group has tested the adsorption of butane and pentane on the Pt(111) crystal surface at 110 K. They have found that preadsorbed oxygen promoted the adsorption of the hydrocarbons and that preadsorbed hydrogen hindered it. Although our experimental temperature was much higher than theirs, for what it is worth, we do have a related tendency, i.e., the oxygen-processed gold surface gave a higher energy transfer efficiency than did the hydrogen-processed surface. Furthermore, they found that the carbonaceous overlayer formed on the metal surface by the pyrolysis of organic materials decreased the reaction rate. This conclusion is parallel with our observations.

Another factor which is worthy of mention is sintering or reorganization of the crystal lattice. The P_c curves in Fig. 6 bend over rather quickly as the temperature was increased, and all three curves approach each other. From estimates of the Tammann temperature²⁴ and the melting point (1336 K) of gold, then in the range 400 - 600 K the crystal lattice of gold may start to become mobile, the surface atoms may exchange with the bulk atoms and at even higher temperature the influence of different processing procedures is more likely to be lost.

It may be useful to point out that the strong collider characteristic of the gold surface at low temperature could in some circumstances be useful for

the estimation of the threshold energy E_0 of some chemical reactions. As a routine method, E_0 is usually derived from the high pressure Arrhenius parameters. Sometimes high pressure experiments give troubles. In that case, it might be a better choice to take advantage of lower pressure and the strong collider character of gold or other surfaces.

Nitromethane

Energy transfer by nitromethane at a silica surface has been studied before by the VEM method.¹¹ Although the products of the reaction were not identified thoroughly, the species were similar to the products reported in the literature²⁵⁻²⁷ for which a C-N bond rupture mechanism has been concluded. When the silica surface was simply seasoned with the reactant itself, as was customary in earlier experiments with hydrocarbons in order to eliminate surface reaction,⁶⁻¹⁰ some evidence of surface catalysis and irreproducibility was exhibited. Processing of the silica by oxygen in fact gave the lowest decomposition rate as well as reproducible data. A higher energy transfer efficiency for nitromethane relative to cyclobutene was found, presumably due to the higher polarity of the former. A threshold energy, $E_0 = 54.4 \text{ kcal mol}^{-1}$, used to fit these experimental results was calculated from Arrhenius parameters in the literature.²⁷

In the gold wire reactor, a pressure of $\sim 1 \times 10^{-4}$ torr nitromethane on variously processed/seasoned surfaces was employed. To process the gold surface, a variety of additional procedures was used: oxidation by oxygen; oxidation followed by exposure to hydrogen, or nitrogen, or argon or xenon; reduction by carbon monoxide, or by nitromethane itself, or by cyclopropane. The processing temperature was 1000-1100 K. Under all of these conditions the gold-nitromethane system exhibited strong catalytic and, more or less ($\pm 50\%$), reproducible characteristics, i.e., the different processing procedures gave no large differences in reactivity in the experimental temperature range. However, the

experimental P_c values were one to two magnitudes higher than the values calculated for a strong collider, based on the threshold of $54.4 \text{ kcal mol}^{-1}$. From 500 K to 900 K, the P_c value increased with temperature. From 900 K to 1100 K, (the highest temperature examined), the P_c curve became flat. This phenomenon is quite different from the behavior of nitromethane at the silica surface.¹¹ In Fig. 7 a graph of results on the cyclopropane-seasoned (at 1000 K) gold wire surface is shown. The experimental points roughly follow a strong collider curve having a threshold energy of $31\text{-}32 \text{ kcal mol}^{-1}$. It is quite evident that the seasoning, resulting in deposition of a graphitic polycyclopropane layer in this case, does not necessarily mask the effect and behavior of the underlying substrate.

Appendix

Vibrational frequencies (cm^{-1}) and parameters used in calculation:

(1) Cyclobutene:²¹

Molecule: 3126, 3058, 2955(2), 2933, 2916, 1566, 1444, 1426, 1288, 1276,
1210, 1186, 1113, 1100, 1074, 986, 875, 850, 846, 800, 640, 635,
325.

Activated complex A: 3015(6), 1340(7), 1005(6), 670(3), 335. $E_0=32.0$ kcal/mol

Activated complex C: 3300(6), 1320(12), 660(5). $E_0=32.4$ kcal/mol; $F=1.3$

(2) Nitromethane:^{11,28}

Molecule: 3048(2), 2965, 1582, 1488, 1449, 1413, 1384, 1153, 1097, 921, 647,
599, 476, internal rotation ($\sigma = 6$)

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- † This work was supported by the Office of Naval Research.
- ‡ Visiting Scholar from Qinghua University, Beijing, P.R.C.
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Figure Captions:

Fig. 1. Comparison of accommodation coefficients.

○, *n*-octane—silica system¹²; ▲, *n*-butane—platinum system⁵;
 □, cyclobutene—silica system, this laboratory.^{7,8,10}

Fig. 2. First order plots, gold finger reactor.

□, oxidized surface; ■, seasoned surface; ○, oxidized-reduced surface.

Fig. 3. The apparent rate constant k vs. the temperature TK for the finger reactor;

□, oxidized surface; ■, seasoned surface; ○, oxidized-reduced surface.

Fig. 4. The single-collision reaction probability P_c for cyclobutene vs. TK for the finger reactor; - - - strong collider curve ($E_0 = 32.0 \text{ kcal mol}^{-1}$);

— strong collider curve ($E_0 = 32.4 \text{ kcal mol}^{-1}$); □, oxidized surface; ■, seasoned surface; ○, oxidized-reduced surface.

Fig. 5. First order plots, gold wire reaction; ○, $C = 10^{-2}$, $T = 1015 \text{ K}$, oxidized-reduced surface; ●, $C = 10^{-3}$, $T = 844 \text{ K}$, seasoned surface.

Fig. 6. The single-collision reaction probability P_c for cyclobutene vs. temperature T in the gold wire reactor; - - - strong collider curve ($E_0 = 32.0 \text{ kcal mol}^{-1}$); — strong collider curve ($E_0 = 32.4 \text{ kcal mol}^{-1}$); □, oxidized surface; ■, seasoned surface; ○, oxidized-reduced surface.

Fig. 7. The experimental, ○, single-collision reaction probability P_c for nitromethane vs. temperature T in the gold wire reactor. The number on every solid curve is the assumed E_0 value (kcal mol^{-1}) used for calculating strong collider curves.

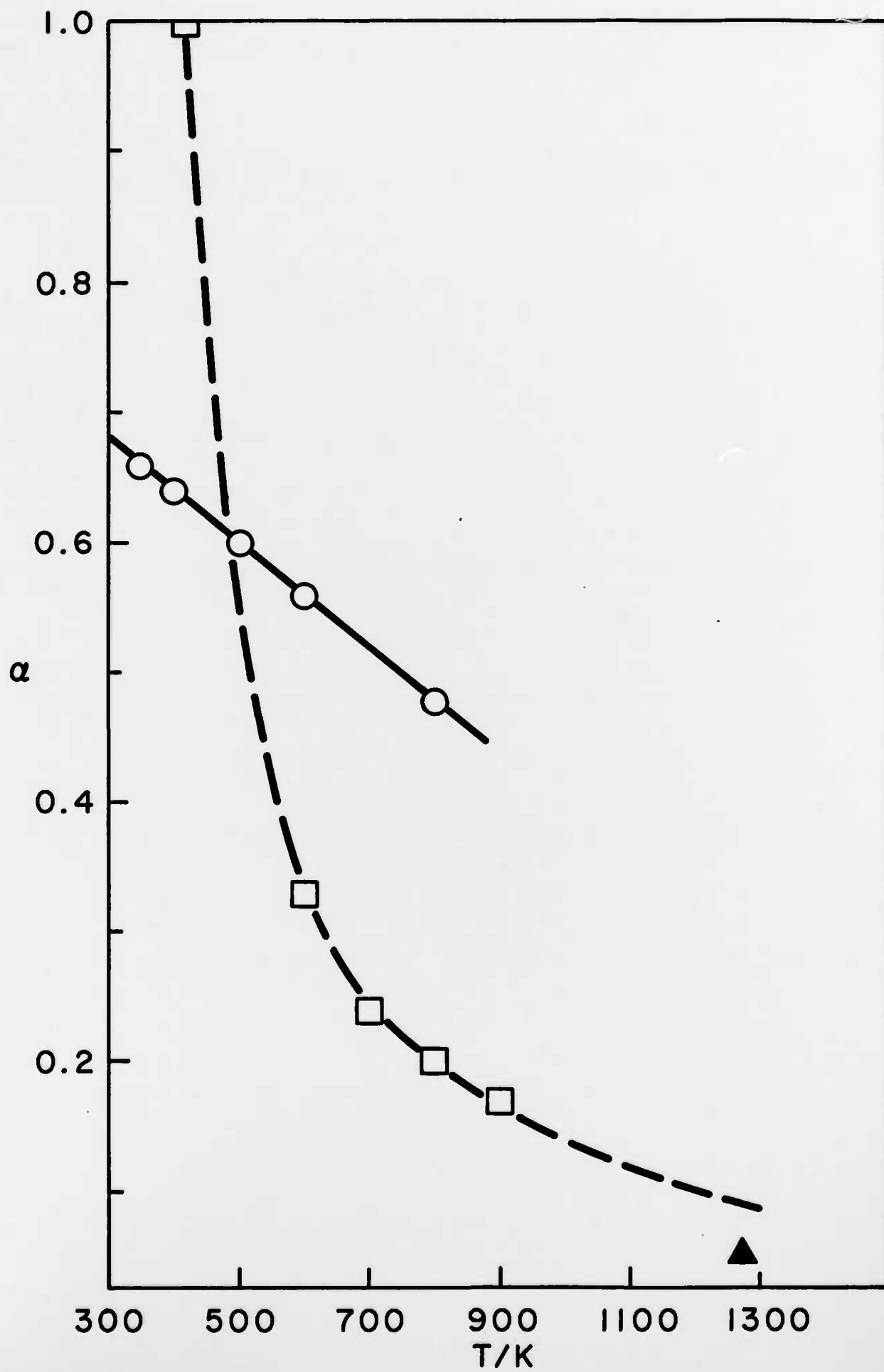


Fig. 1

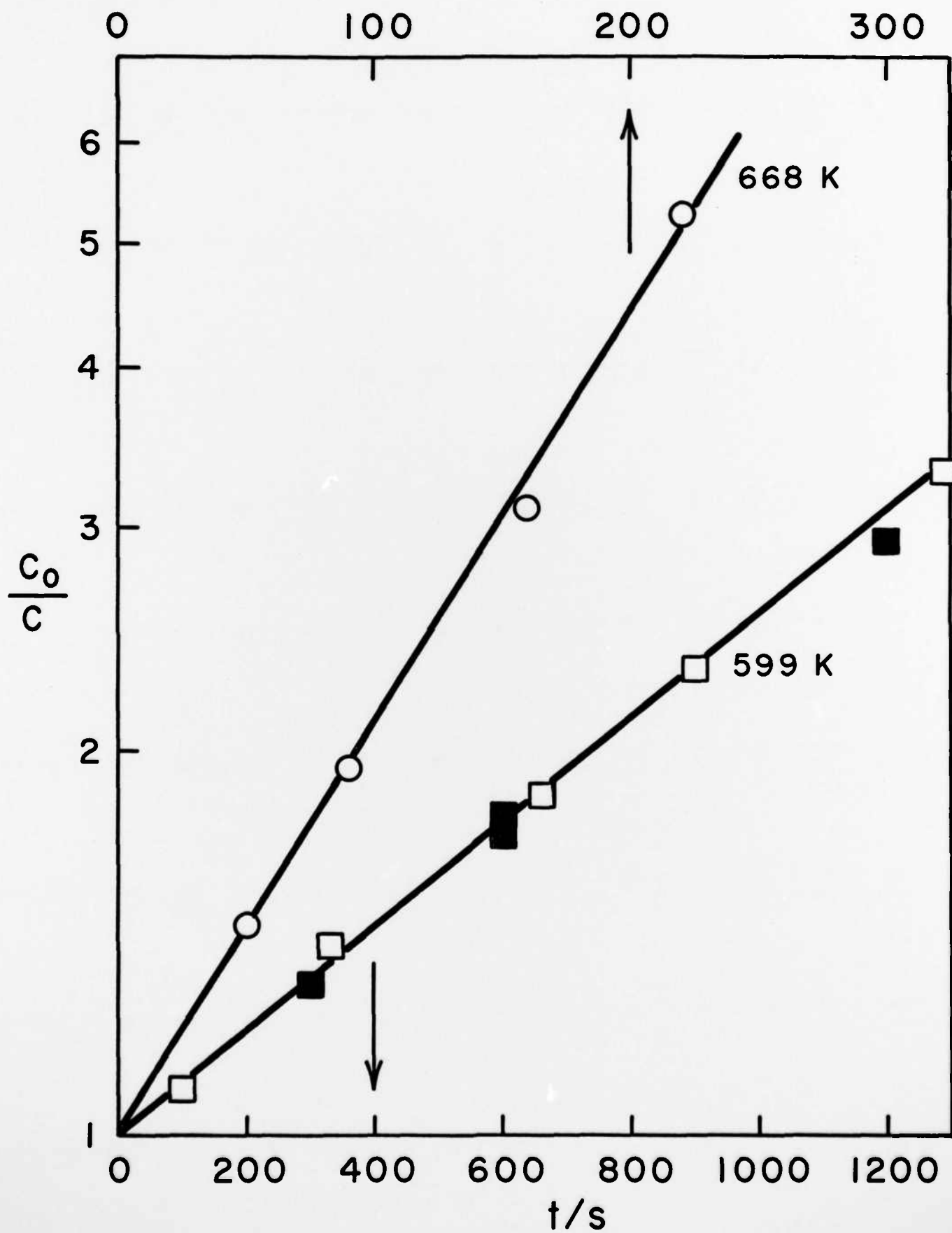


Fig. 2

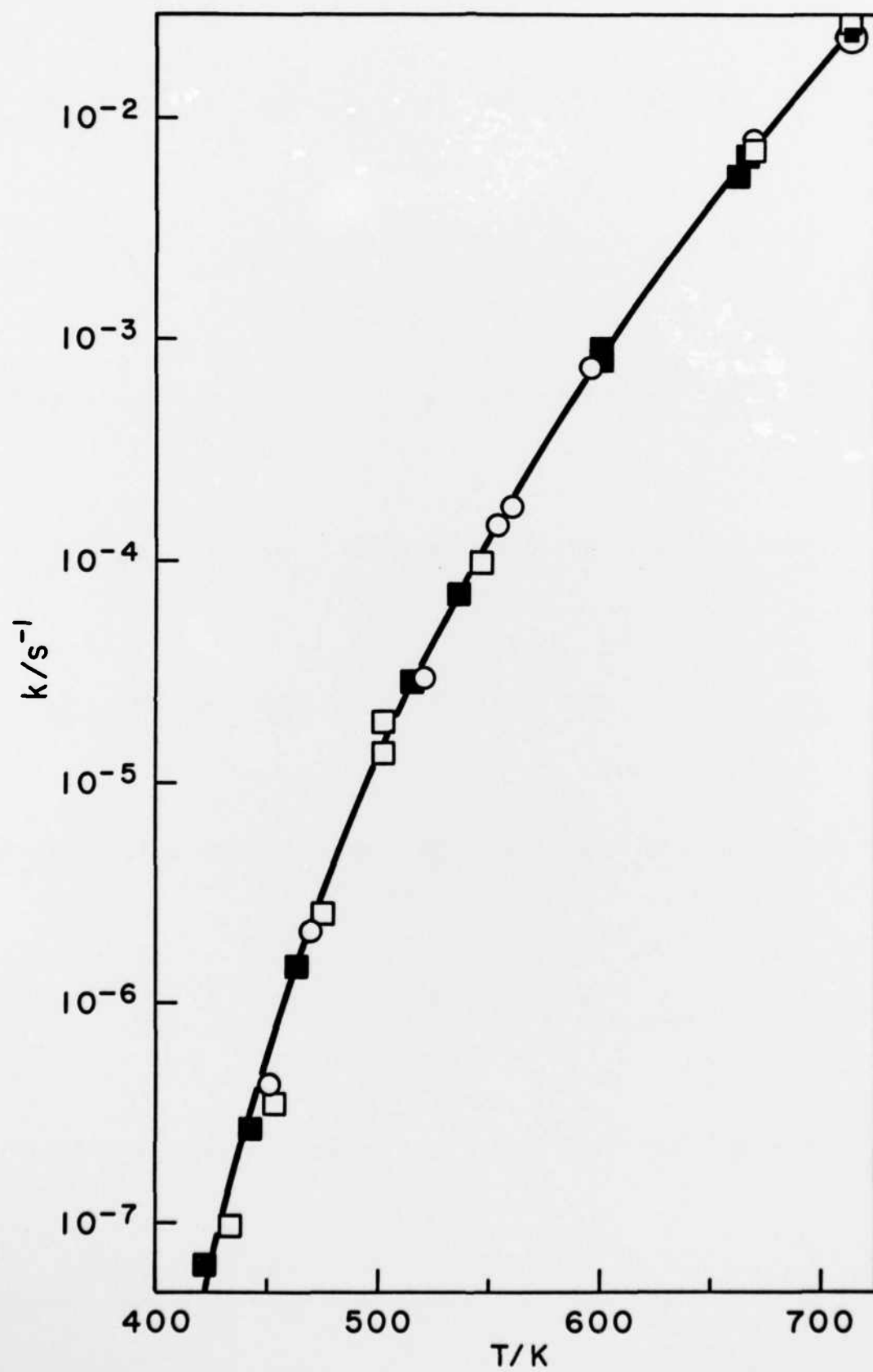


Fig 3

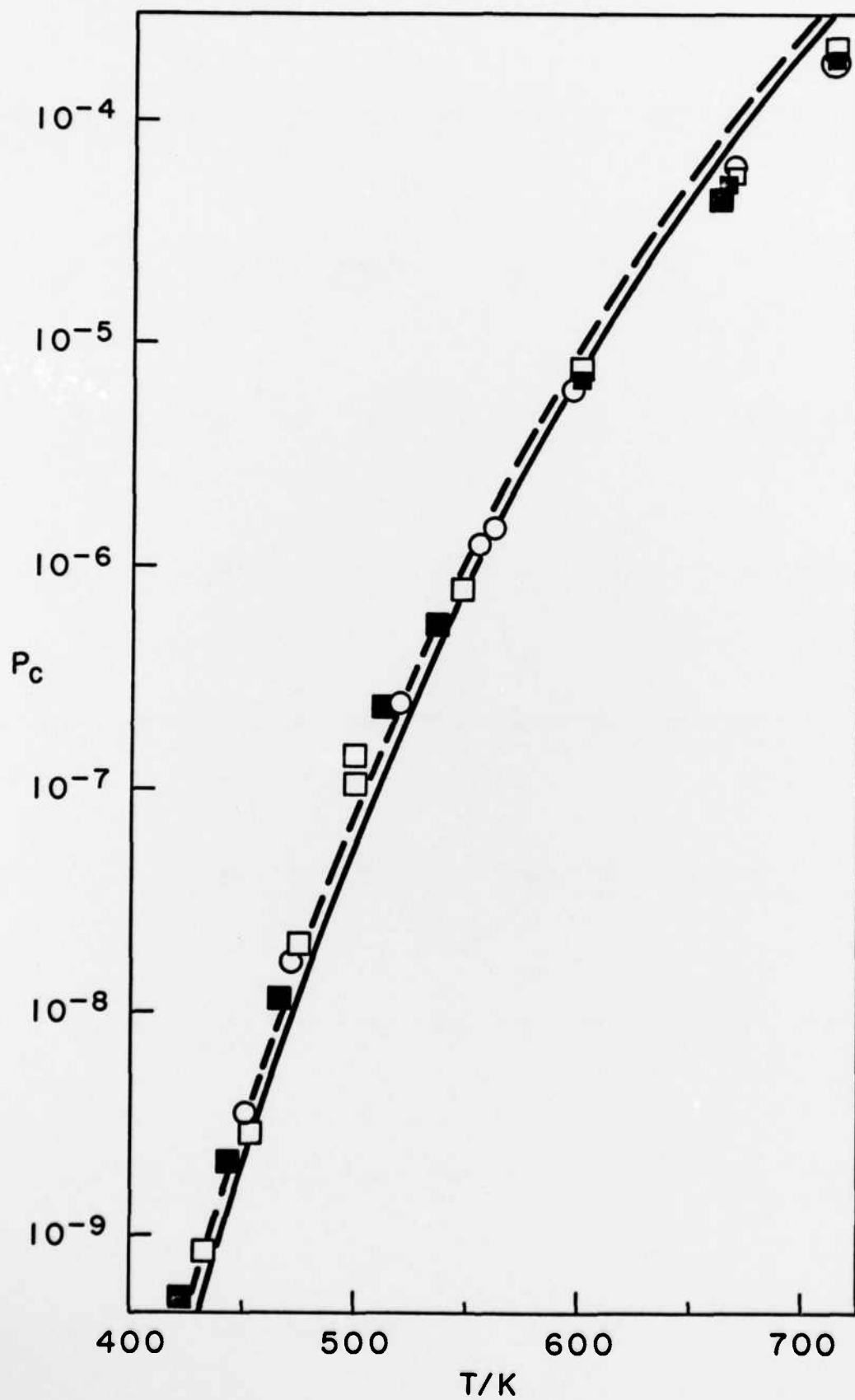
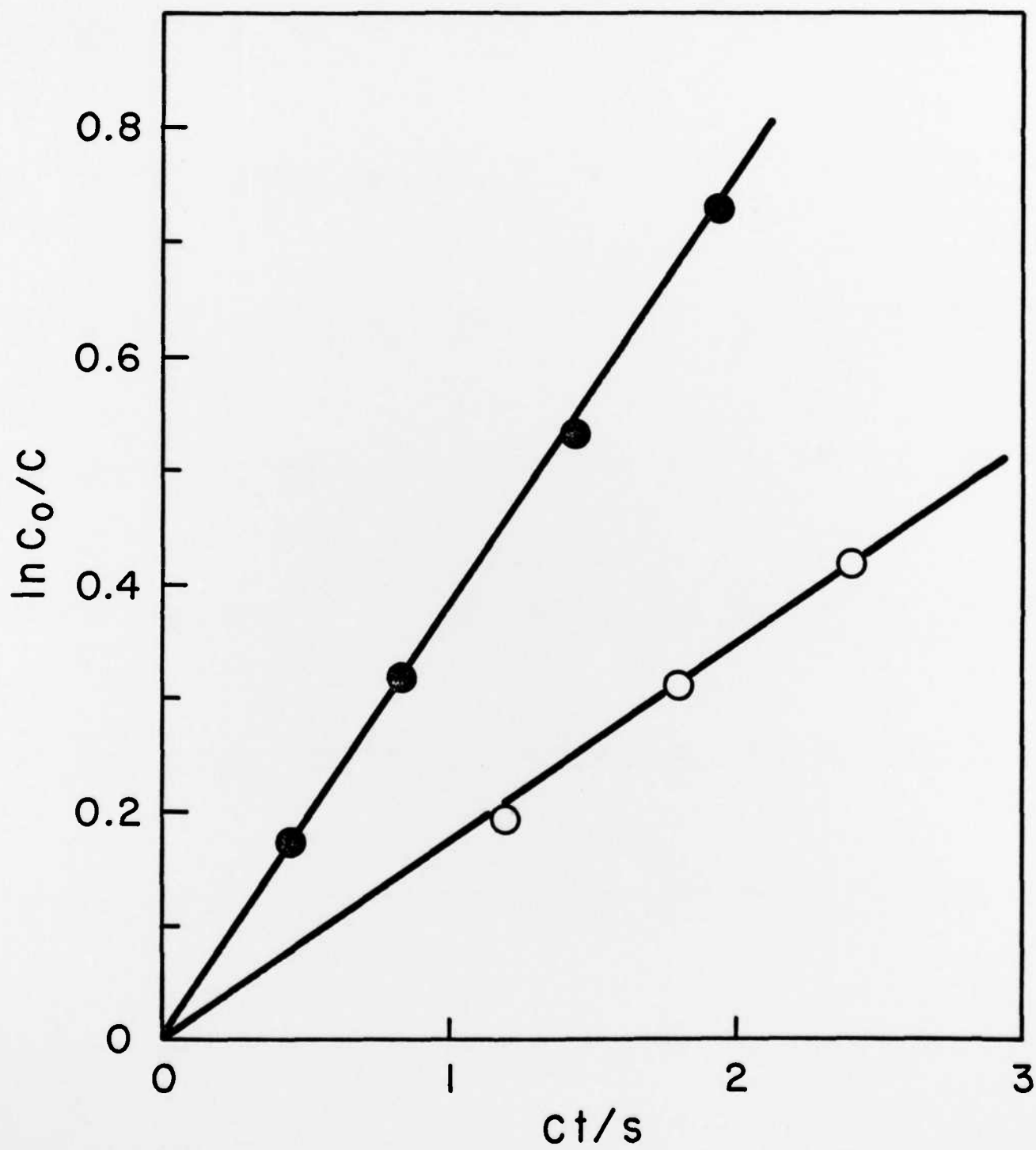


Fig. 4



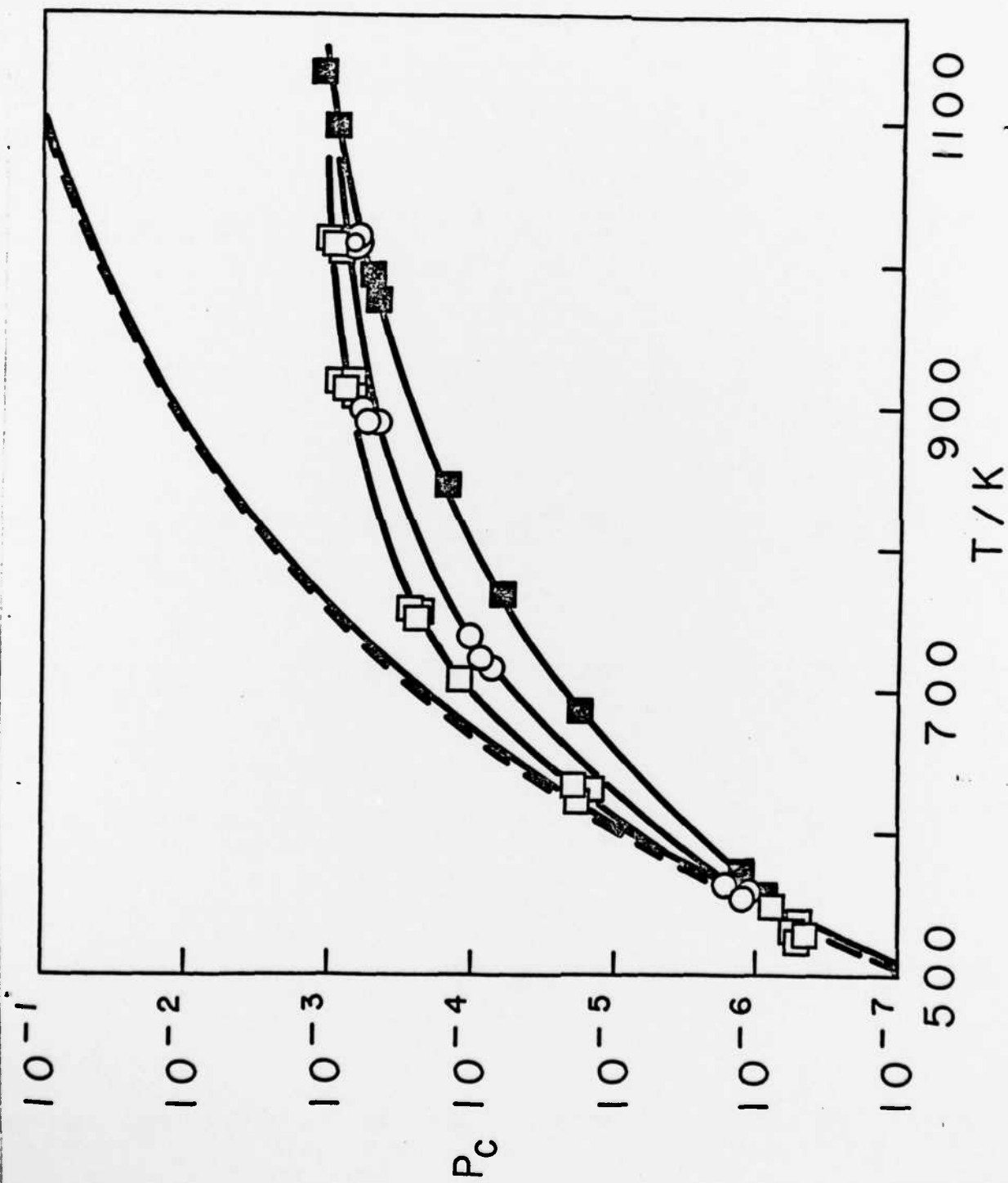
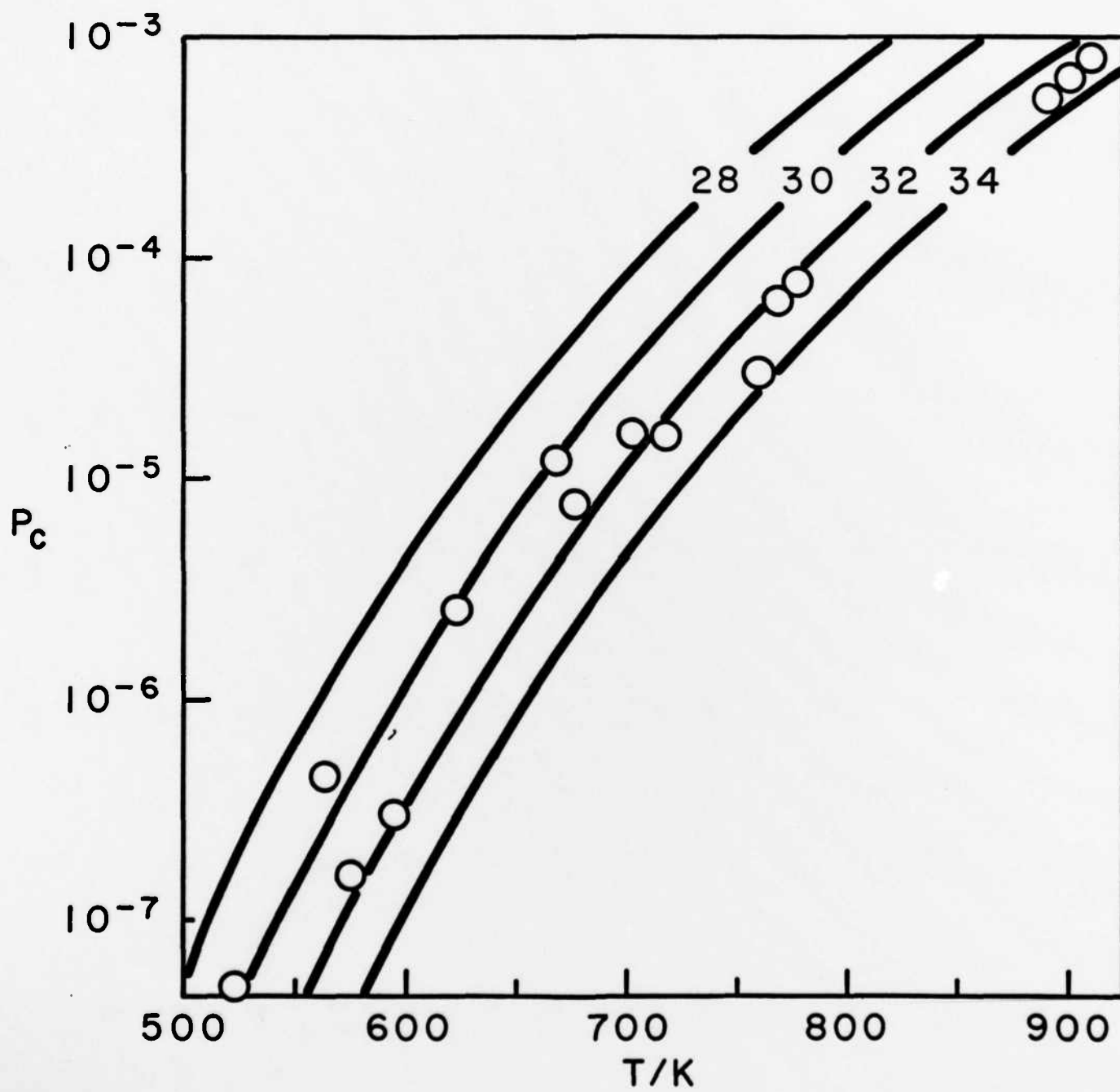


Fig. 6



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